Preparation and Characterization of Melamine-Formaldehyde Resin Microcapsules Containing Fragrant Oil

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Abstract In this study, melamine-formaldehyde microcapsules were prepared via *in situ* polymerization using peppermint oil as a core material, melamine-formaldehyde as the wall material, Tween 20 as the emulsifier, and poly (vinyl alcohol) as a protective colloid. The melamine-formaldehyde microcapsules prepared in this study were then evaluated with regard to their structures, thermal properties, particle size distributions, morphologies, and release behaviors.

Keywords: fragrant oil, *in situ* polymerization, melamine-formaldehyde, microcapsule, peppermint oil

INTRODUCTION

Microcapsules have been employed in a variety of fields, including carbonless copying papers, adhesives, cosmetics, insecticides, drug carriers, and pharmaceutical applications [1-4]. They are a form of microscopic contained, and are used to encapsulate a selected functional material in a shell of polymer ranging in size from several nanometers to micrometers. These capsules are typically composed of polymer matrices, which allow for the release of functional substances, or for the protection of them from the outer environment [2]. Microcapsules perform a variety of functions, including the release of functional substances at a controlled speed and the protection of unstable materials within a particular environment [5]. As a result of these qualities, microencapsulation techniques have been extensively employed in textile industries for the preparation of functional fibers [1].

Several microencapsulation techniques, including the chemical method (*in situ* polymerization and interfacial polymerization), the physical-chemical method (coacervation), and the mechanical-physical method (spray encapsulation), have thus far been developed [6,7]. Among these, *in situ* polymerization and interfacial polymerization methods have become the most commonly used methods for the preparation of microcapsules and functional fibers. In interfacial polymerization, monomers are added to a dispersion medium and a dispersed core material, and polymerization occurs at the interface. *In situ* polymerization method results in the formation of a wall via the addition of a reactant into either the interior or the exterior of the core material [8,9].

In this study, microcapsules were prepared via *in situ* polymerization, as this method has several advantages over others, including high yield encapsulation, inexpensive preparation cost, and ease of regulation of the encapsulation process [10]. In order to prepare the microcapsules, melamine-formaldehyde resin was used as a wall material, thereby enhancing the durability of fragrance onto the fibers. The objective of this study is to investigate the *in situ* polymerization of melamine-formaldehyde (M-F) microcapsules via assessment of surface functionality, thermal properties, and morphology. In service of this objective, hydrophobic peppermint oil was utilized as a model fragrant oil and a core material.

MATERIALS AND METHODS

Materials

Melamine and 37% formaldehyde, which were utilized as wall materials in this study, were obtained from Sigma-Aldrich of USA with no further purification. Peppermint oil, which was used as a core material, was purchased from Bolak of Korea. Tween 20, used as an emulsifier, and acetic acid and NaOH, which were used as pH controllers, were obtained from Daejung Chem. of Korea, and poly (vinyl alcohol) (PVA), used as a protective colloid, was acquired from Wako Pure Chem. of Japan. All chemicals used in this work were of reagent grade.

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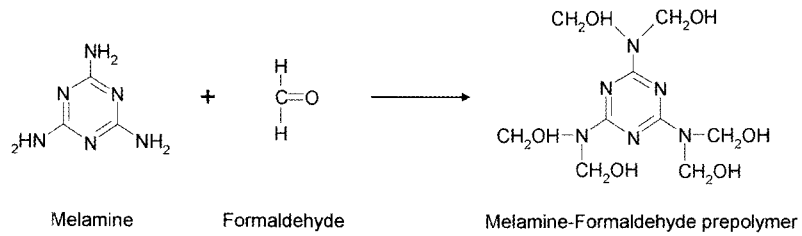

Fig. 1. Suggested reaction mechanism for melamine and formaldehyde.

Preparation of Melamine-Formaldehyde Prepolymer

Melamine (0.2 M) and 37% formaldehyde (0.6 M) in 50 mL of distilled water were adjusted to pH 8.8 ± 0.1 using 0.5 M NaOH solution. The melamine-formaldehyde (M-F) prepolymer was prepared under alkaline conditions. The M-F prepolymer was prepared via 1.5 h of stirring, at a temperature of between 87 and 90°C.

Emulsification of Peppermint Oil

After the Tween 20 (2%, w/v) was dissolved in 50 mL of distilled water, peppermint oil was added to the solution as core material. The peppermint oil emulsion was prepared using a homogenizer at 13,000 rpm and room temperature.

Preparation of Microcapsules

Microencapsulation of peppermint oil was conducted in a 500-mL four-neck flask via *in situ* polymerization. After the prepared emulsion was placed in the flask, the emulsion solution was adjusted to a pH of 8.0 via the addition of 0.5 M NaOH solution. The M-F prepolymer was then added to the flask, followed by stirring at 600 rpm at 50°C. The pH of the solution was then lowered gradually from 8.0 to 6.5 over 1.5 h of reaction time, in order to separate the M-F prepolymer from the aqueous phase. After the addition of 0.002 M of PVA as a protective colloid, the M-F prepolymer attached to the surface of the peppermint oil was cross-linked, and then solidified via pH control. The cross-linking reaction was conducted for 30 min at pH 5.5~6.0 and for 1 h at pH 5.0. During the cross-linking reaction, the temperature was adjusted to 65°C. After the completion of the microencapsulation reaction, the resultant microcapsules were collected and washed in 30% (w/v) ethanol solution and distilled water, in order to remove any unreacted formaldehyde and free peppermint oil remaining on the surfaces of the microcapsules. The capsules were then dried for 24 h *in vacuo* at room temperature.

Characterization of Microcapsules

The surface functional groups of peppermint oil and M-F microcapsules were examined using a Nicolet 520P FT-IR spectrophotometer. The morphology of the microcapsules was investigated using an Olympus optical microscope and a Jeol Model JSM-5400 scanning electron microscope (SEM). For SEM analysis, the microcapsules were scattered onto double-sided tape, sputter-coated with gold, and examined under a microscope. The mean particle size and size distribution of the microcapsules were determined using an Otsuka Model ELS-8000 particle size analyzer [11]. The thermal stability of the polymer and microcapsules was evaluated with a Mettler Model TGA/SDTA851 thermogravimetric analyzer (TGA). The samples, at 5 mg each, were heated to 600°C at a rate of 10°C/min.

Release Test

The microcapsules were placed in a drying oven for 5 days at 25 and 40°C in order to quantify the decrease in the weight of peppermint oil released from the M-F microcapsules. The release rate (%) was calculated via the following equation, and the data were expressed as the residual weight of the microcapsules.

$$\text{Release rate (\%)} = \frac{A-B}{A} \times 100$$

A: the weight (g) of microcapsules before release test
B: the weight (g) of microcapsules after release test

RESULTS AND DISCUSSION

Structure of Microcapsules

Fig. 1 shows the suggested reaction mechanism of the M-F prepolymer. The new C-N bond and O-H group can be seen in the M-F prepolymer. Fig. 2 shows the FT-IR spectra of peppermint oil as core material and the M-F microcapsules containing fragrant oil. As shown in Fig. 2A, the peaks responsible for menthol and menthone, the principal ingredients of peppermint oil, were observed. The O-H peaks of menthol were detected at 3,427 cm^{-1}, 1,045 cm^{-1}, and 1,025 cm^{-1}, the $-CH_3$ peaks appear at approximately 2,924 cm^{-1}, 1,456 cm^{-1}, and 1,368 cm^{-1}, and C=O peak of menthone appears at approximately 1,700 cm^{-1}. According to Fig. 2B, the O-H stretching vibration at 3,340 cm^{-1}, C-H stretching vibration at 2,949 cm^{-1}, N-H bending vibration at 1,559 cm^{-1}, C-N absorption band at 1,354 cm^{-1}, and C-O stretching vibration at 1,165 cm^{-1} were all observed. A $-CH_3$ peak at 2,924 cm^{-1} and a C=O peak at approximately 1,700 cm^{-1} were also observed. These results represent the formation of the M-F prepolymer, and the absorption bands

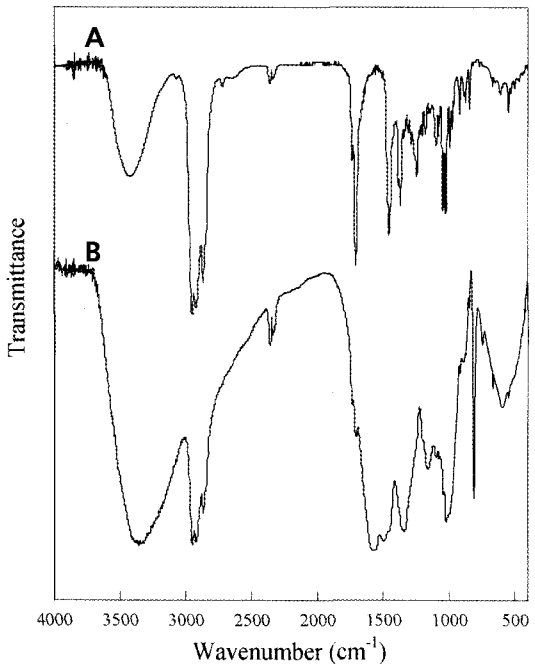

Fig. 2. FT-IR spectra of melamine-formaldehyde resin microcapsules: (A) peppermint oil and (B) melamine-formaldehyde resin microcapsule containing peppermint oil.

specific to peppermint oil and M-F resin were also detected in the microcapsules. In accordance with the FT-IR spectral findings, it can be deduced that the core material and the wall material of microcapsules were peppermint oil and M-F resin, respectively.

Thermal Properties of Microcapsules

TGA thermograms of M-F prepolymer and of the M-F microcapsules containing peppermint oil are shown in Fig. 3. Substantial weight losses were observed at 420°C in both the M-F prepolymer and M-F microcapsules, probably due to the degradation of the M-F resin. However, the weight loss of the M-F microcapsules was found to be approximately 20% greater than that of the M-F resin. This result implies that an approximately 20% residual weight difference should be observed as the result of temperature change in the M-F resin and the peppermint oil-containing M-F microcapsule. According to the TGA data, the prepared M-F microcapsules normally contained approximately 20% peppermint oil. Hong and Park [1] assessed the loading efficiency of the M-F resin microcapsules via analyses of the loading amount of migrin oil in the microcapsules, using 1,4-diaminoanthraquinone (DAA) as a model core material with the same molecular weight as migrin oil, and concluded that the loading amount of migrin oil corresponded with the TG results. They also reported that the loading efficiency of migrin oil in the M-F resin microcapsules was about 87%. The loading efficiency of peppermint oil may differ from that of migrin oil, due to differences in the molecular weights of the oils. However, the loading efficiency of

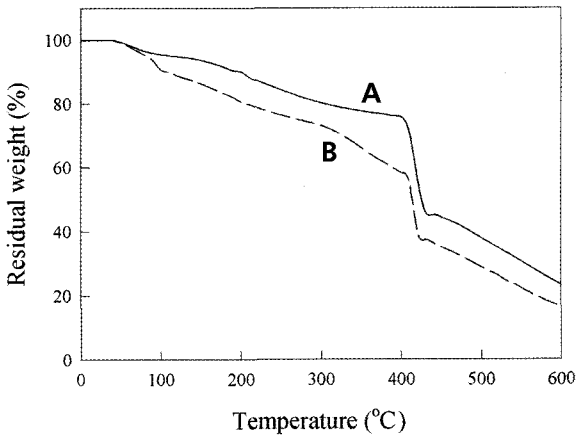

Fig. 3. TGA thermograms of melamine-formaldehyde resin microcapsules: (A) melamine-formaldehyde prepolymer and (B) melamine-formaldehyde resin microcapsule containing peppermint oil.

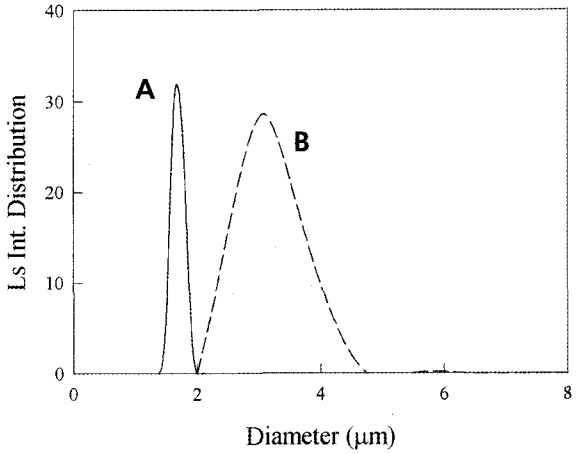

Fig. 4. Particle size distribution of melamine-formaldehyde resin microcapsules containing peppermint oil: (A) 13,000 rpm and (B) 15,000 rpm.

peppermint oil would be expected to be higher than that of migrin oil, because the molecular weight of peppermint oil (Mw 156.27) is less than that of migrin oil. According to the results of our thermal analyses of M-F resin microcapsules, the loading amount of peppermint oil should be approximately 20% (w/w).

Particle Size Distribution

Fig. 4 shows the particle size distribution of the prepared M-F microcapsules containing peppermint oil. The particle size distribution of the microcapsules was quite narrow when stirred at a rate of 13,000 rpm, and the mean diameter of the particles was less than 2 μm. However, when the microcapsules were prepared via stirring at 15,000 rpm, the particle size distribution of the microcapsules became broader, and they were larger than those observed in the microcapsules prepared at a stirring rate

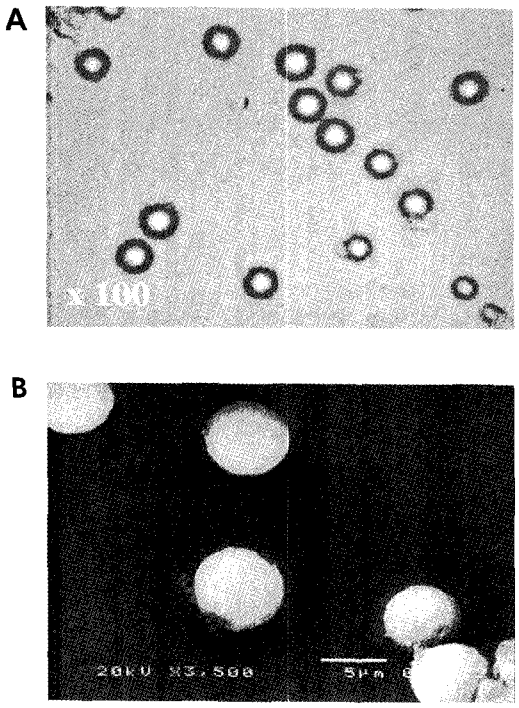

Fig. 5. Image photographs of melamine-formaldehyde resin microcapsules containing peppermint oil: (A) optical micrograph (× 100) and (B) scanning electron micrograph (× 3,500).

of 13,000 rpm. It appears likely that the distribution of the M-F microcapsules depends primarily on the properties of the stirring rate in the emulsion. This finding is consistent with the results of a previous study conducted by Park *et al.* [9], who reported that the size of microcapsules became larger due to high agitation rates, because the emulsion particles consequently break and reagglomerate, and also that the stability of o/w emulsions might be reduced as the result of high agitation rates.

Morphologies

The photographs of surface morphologies of the M-F microcapsules prepared at 13,000 rpm are shown in Fig. 5. As shown in the figures, surface morphology of the microcapsules seems to be quite smooth, which may enable the microcapsules to be sustained releasable membrane. As a similar investigation, Hong and Park [1] previously reported that the surface morphology of the microcapsules had sustained releasable membrane due to its great surface smoothness. Therefore, the M-F microcapsules should prove useful with regard to the protection and sustained release of interior fragrant oils, as a result of their smooth surface morphology.

Release Behavior

Fig. 6 shows the release behavior after release tests conducted for 5 days at 25 and 40°C, in order to determine the degree of the release rate of the core material within the M-F microcapsules. The amounts of core material released during the experiments were significantly less than 0.1% at both 25 and 40°C, for up to 120 h. This result implies that the peppermint oil-containing M-F resin microcapsules prepared in this study were very durable, and also possessed a rather long shelf-life. Therefore, the M-F microcapsules prepared in this study appeared to release their fragrance via the destruction of the walls, rather than by passive diffusion, under room temperature conditions. In accordance with this observation, it can be concluded that M-F microcapsules might prove useful in the preparation of functional fibers, as a result of both their substantial durability and reasonable heat-resistance characteristics.

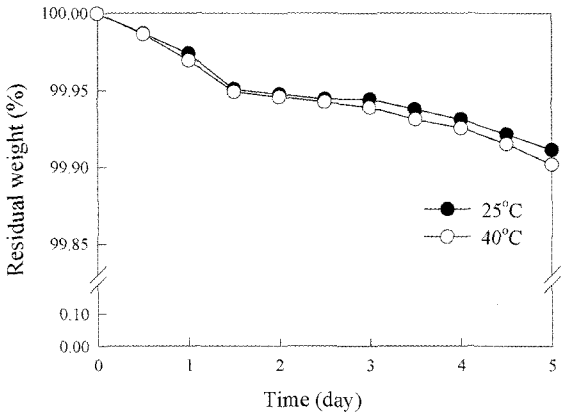

Fig. 6. Residual weight of melamine-formaldehyde resin microcapsules containing peppermint oil during 5-day release test at 25 and 40°C.

CONCLUSIONS

Melamine-formaldehyde microcapsules containing fragrant oil were prepared via *in situ* polymerization in this study, and these capsules were evaluated with regard to size distribution, thermal properties, morphologies, and release behavior. The prepared microcapsules contained approximately 20% peppermint oil, as derived from the differences in weight loss in the prepolymer and microcapsule. The particle sizes of the microcapsules appeared to be dependent on the stirring rate. The peppermint oil-containing melamine-formaldehyde resin microcapsules evidenced smooth surface morphologies, and proved capable of preserving the encapsulated fragrant oils for sufficient periods of time.

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